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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

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MAGNESIUM COMPOUNDS

(OTHER THAN MAGNESITE)

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PAUL M. TYLER

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

MAGNESIUM COMPOUNDS (OTHER THAN MAGNESITE)[1]

By Paul M. Tyler[2]

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[1] - The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6406."

[2] - Chief engineer, rare metals and nonmetals division, U. S. Bureau of Mines.

INTRODUCTION

In point of tonnage the most important item considered in the present paper is precipitated magnesium carbonate used principally in pipe and boiler coverings. Consideration is also given to calcined magnesia and to the chloride, sulphate, and other salts of magnesium. The natural compounds--magnesite, dolomite, and brucite--and magnesium metal are discussed or will be discussed in other publications of the Bureau of Mines.

Magnesite, the natural carbonate of magnesium, and dolomite or high magnesian limestone, a natural mixture of the carbonates of magnesium and calcium, are the leading mineral sources of magnesium, and either in the raw or burned condition these minerals are extensively employed in industry, notably in refractories and in cements and flooring compositions. Brucite, a natural hydrate of magnesium, is a potential commercial source of the element and its compounds. Natural brines, more particularly the mother liquors remaining after the recovery of common salt from salt wells or sea water, and also certain deposits of solidified salts such as the famous beds at Stassfurt now constitute the leading sources of magnesium metal and of several of its salts.

Magnesium is one of the major constituents of the earth's crust; it is the eighth most abundant element.3/ Since it is so widely distributed a choice of raw material for its chemical compounds is largely a matter of cost, and this in turn is determined in a large measure by geological conditions. In the eastern United States, for example, the technical carbonate for pipe coverings is obtained exclusively from dolomite, but in California it is made from magnesite. Locally it may also be manufactured from natural salts. Before the World War a large part of the magnesium salts used in this country was imported from Europe and the remainder was made principally from crude magnesite which was imported principally from Greece. Subsequently and more especially following the passage of the Tariff Act of 1922, caustic calcined magnesite was used instead of crude magnesite by many chemical manufacturers. Since the calcined material weighs only about one-half as much as the crude rock and since it is much more readily dissolved, the saving in freight and other advantages more than compensate for the higher cost. According to figures obtained by the United States Tariff Commission4/ covering the first nine months of 1923, it would appear that the annual consumption of caustic magnesite for purposes other than stucco and flooring is approximately as follows:

	Short tons
Rubber trade	800
Insulation	1,100
Chemicals	4,300
Not determined5/	2,500
Total	8,700

As shown in the table on page the quantity of dolomite sold or used by producers in the United States for the manufacture of basic magnesium

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3/ Clarke, F. W., Data of Geochemistry: U. S. Geol. Survey, Bull. 770, 1924, p. 29.

4/ U. S. Tariff Commission Preliminary Statement Issued to the Trade: May 19, 1926, p. 4.

5/ May include some magnesite ultimately consumed in stucco or flooring.

carbonate has averaged during the last five years for which statistics are available approximately 84,000 short tons. In addition crude dolomite has been employed for the manufacture of carbon dioxide, which may be considered a chemical use. The Bureau of Mines is not at liberty to publish figures covering the consumption of dolomite for this latter purpose after 1926, in which year 16,520 tons of dolomite valued at $31,424 were sold by domestic producers for the manufacture of carbon dioxide. There are only two producers, one of whom furnishes stone to a California chemical firm which uses the gas in the manufacture of soda products (e. g. sodium carbonate), and the other, a Georgia firm, employs dolomite as a source of carbon dioxide for use in making carbonated beverages. Dolomite has been proposed as a source of gas for the manufacture of "dry ice," but the latter has so far been made principally from burning coke.

Mention may be also made of the use of high magnesium lime for sulphite paper mills which purchase from 50,000 to 75,000 or more short tons of calcined dolomite annually.

Production data on this group of industries are incomplete. As has been already noted, the Bureau of Mines obtains figures covering the quantity of crude dolomite used in the manufacture of technical carbonate, but there is no record of the volume of the product or of the increasing quantity of other magnesium-bearing materials that are used for this purpose. The Bureau of the Census groups this material in finished form under the general category: "Steam and other packing, pipe and boiler covering, and gaskets, not made in textile mills," and there is possibly a further overlap with the products of the asbestos industry.

With respect to the production of magnesium salts, largely magnesium sulphate and chloride, from natural salts and bittern waters in the United States, the Bureau of Mines is at liberty to publish total figures, but since there are often less than three producers each of magnesium sulphate and magnesium chloride the bureau can not publish production figures separately. The Bureau of the Census gives figures for the output of epsom salts from natural deposits and by chemical processes but groups the chloride and oxide with numerous minor compounds. The Census data for recent years follow:

Output of Epsom Salts from Natural Deposits and by Chemical Processes
(Compiled by Bureau of the Census)

	1927	1925	1923	1921
Magnesium sulphate (Epsom salt):				
Number of establishments	8	11	12	12
Tons	27,665	23,428	20,676	14,923
Value	$1,141,633	$1,219,177	$851,103	$753,822
Other salts and compounds:				
Value	1,548,508	2,631,331	2,223,163	1,445,465

Next to the United States, Germany is undoubtedly the largest producer of magnesium salts. In 1929 it was reported that 42,999 metric tons of magnesium chloride and 100,869 metric tons of magnesium sulphate were produced as by-products of the potash industry; the corresponding figures for 1928 were 36,585 tons and 93,942 tons, respectively. The German magnesium salt industry has been described by Daugherty:[6]

> Carnallite ($KCl.MgCl_2.6H_2O$) is one of the chief salts occurring in Germany's natural soluble potash deposits. Before the war carnallite was worked extensively for recovery of its potassium chloride content for fertilizer. A small fraction, according to market demand, was processed for commercial magnesium chloride and bromine, and some 800,000 metric tons of magnesium chloride were discarded annually. The waste liquors containing this compound were dumped in the rivers of central Germany and created a serious stream pollution problem, while the costs of processing carnallite were greater than for sylvinite, or hard salts, and the process more complicated.
>
> In 1913 Germany mined 5,486,000 tons of carnallite, which represented 47 per cent of the crude potash mined that year. Since the war, much less carnallite has been mined and more of the salts of higher potash content. In 1927 only 1,773,200 tons of carnallite were mined, which was 16 per cent of the total German potash recovered in that year. The same condition applied in 1928.
>
> Carnallite is used for local magnesium chloride manufacture and for magnesium metal. Two or three mines sell their output of specially pure carnallite to the Griesheim Elektron works for electrolytic production of magnesium for its light metal alloy, Elektron, which has a 90 per cent magnesium content. Carnallite producers dispose of about 50,000 tons of solid magnesium chloride annually in other ways and 5,000 tons in 12 per cent liquid form. Only solid magnesium chloride enters export.
>
> Producers are combined in the magnesium chloride syndicate, Berlin, concurrent with the rock salt and bromine syndicates. Rock salt is produced with potash and bromine by treatment of carnallite liquor with chlorine.
>
> Hard salt is a mixture of sylvin (KCl), kieserite ($MgSO_4.H_2O$), rock salt, and anhydrite ($CaSO_4$). Kieserite, as noted, is practically pure magnesium sulphate. Both are prominent in German potash deposits. While these are raw material for potassium chloride fertilizer, they furnish an oversupply of magnesium sulphate, of which some 125,000 tons enter the market annually as bitter salts (the technical grade) or Epsom salts (pharmaceutical grade). Much magnesium sulphide is lost in waste liquors; before the war some 100,000 tons were dumped annually.

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[6] Daugherty, William T., German Chemical Development in 1928: U. S. Bur. For. and Dom. Com. Trade Information Bull. 605, 1929, pp. 24-25.

MAGNESIUM CARBONATE, PRECIPITATED

Description and Uses

Magnesium carbonate is a white, bulky powder, insoluble in water. The ordinary grade, known as technical carbonate, is a basic carbonate; the composition varies somewhat according to the method of manufacture but is approximately expressed by the formula, $4MgCO_3.Mg(OH)_2.5H_2O$. In the United States, at least, about 90 per cent of the output is used in the form of "85 per cent magnesia," a non-heat-conducting covering for steam pipes, boilers, and all kinds of heated surfaces. Specifications for this insulating mixture call for a combination containing "not less than 95 per cent magnesia and asbestos fiber, of which at least 85 per cent of the whole shall be said magnesia" (i.e. carbonate).

The same material is also known as "block magnesia" and in pharmacy is described as "magnesia alba." It is used directly in the rubber trade as an accelerator, and it is a constituent of some paints and certain pharmaceutical preparations. It is used in varnish, glass, printing ink, cosmetics, table salt, toothpaste, etc.

The ordinary variety is a "light carbonate" (terra alba levis), but by varying the method of manufacture a denser form or "heavy carbonate" (terra alba ponderosa) may be obtained. The formula of the latter compound, as sometimes given, contains one less molecule of water than the light carbonate. The light and heavy carbonates, when calcined, yield light and heavy varieties of the oxide, or calcined magnesia (magnesia usta levis or magnesia usta ponderosa).

Methods of Production

The basic carbonate may be obtained by precipitation of either the commercial sulphate or the chloride of magnesium with sodium carbonate. By conducting the precipitation at a higher temperatures, adding one volume of a cold saturated solution of sodium carbonate to a boiling mixture containing one volume of a saturated solution of magnesium sulphate in 30 volumes of water, a precipitate of heavy carbonate is obtained. This precipitate is washed with hot water and dried at 100° C.

Both in England and in the United States, however, the great bulk of the production is made from dolomite by the method originally patented by Pattinson. The raw dolomite mixed with coke is lightly calcined in a kiln and then treated with water and carbon dioxide under a pressure of 5 to 6 atmospheres for a fairly long period. The newly formed carbonate of magnesia is thereby converted into the soluble bicarbonate, and as long as any magnesium carbonate remains undissolved, the calcium carbonate remains unattacked and may be separated by filtering. By boiling the filtrate and removing the carbon dioxide, magnesium carbonate is precipitated and subsequently removed and dried. The carbon dioxide required for digesting the calcine is furnished by the kilns, and the calcium carbonate removed by the first filtration may be sold for the uses of precipitated chalk.

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The general flow sheet of the process as constructed by the short-lived Magnesia Association of America is given on the accompanying chart (fig. 1).

Magnesium carbonate can also be made from sea water. The mother liquor (bittern) obtained after abstraction of common salt is treated with milk of lime to precipitate magnesium hydroxide, which is allowed to settle. After decanting the supernatant liquid the precipitate is stirred up with water and agitated while a stream of carbon dioxide is passed into the mixture.

Domestic Production

Manufacturers of basic magnesium carbonate do not report their output of finished products, but for a number of years the crude dolomite used for this purpose has been reported to the Bureau of Mines. On the basis of these figures, making a rough estimate to cover the production of carbonate from magnesite and sources other than dolomite, it would appear that the dolomitic output of technical carbonate ranges from 50,000 to 75,000 short tons annually. According to a brief presented by domestic manufacturers to the Ways and Means Committee[7] in 1929, the estimated number of employees engaged in the production of magnesium carbonate and its manufactures in the United States is 10,000, and the approximate pay roll is estimated at the high figure of $25,000,000 annually.

The industry is centered largely in Pennsylvania, New Jersey, Ohio, and California. The manufacturers of the carbonate utilize most of their product in their own plants for the manufacture of boiler coverings and molded insulations. The same manufacturers also produce a variety of asbestos goods and similar heat-resisting materials.

Dolomite sold or used by producers in the United States for manufacture of basic magnesium carbonate, 1916-1929[1]

Year	Short tons	Value	Year	Short tons	Value
1916	80,867	$80,595	1923	116,410	$146,337
1917	73,214	89,189	1924	98,160	129,390
1918	90,989	126,255	1925	98,980	131,440
1919	62,652	82,619	1926	72,850	110,560
1920	57,300	107,107	1927	69,940	115,932
1921	32,050	60,648	1928	94,200	122,260
1922	53,170	79,313	1929	84,750	129,380

[1] Data compiled by A. T. Coons, U. S. Bureau of Mines.

Imports

In the five-year period 1909 to 1931, the imports of precipitated magnesium carbonate ranged from 101,393 pounds valued at $4,855 in 1908, to 42,325 pounds valued at $2,509 in 1909. Statistics of imports for 1919 to 1929 are as follows:

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[7] House of Representatives, Committee on Ways and Means, Tariff Hearings: 70th Congress, 2nd Sess., 1929, vol. 1, pp. 553-4.

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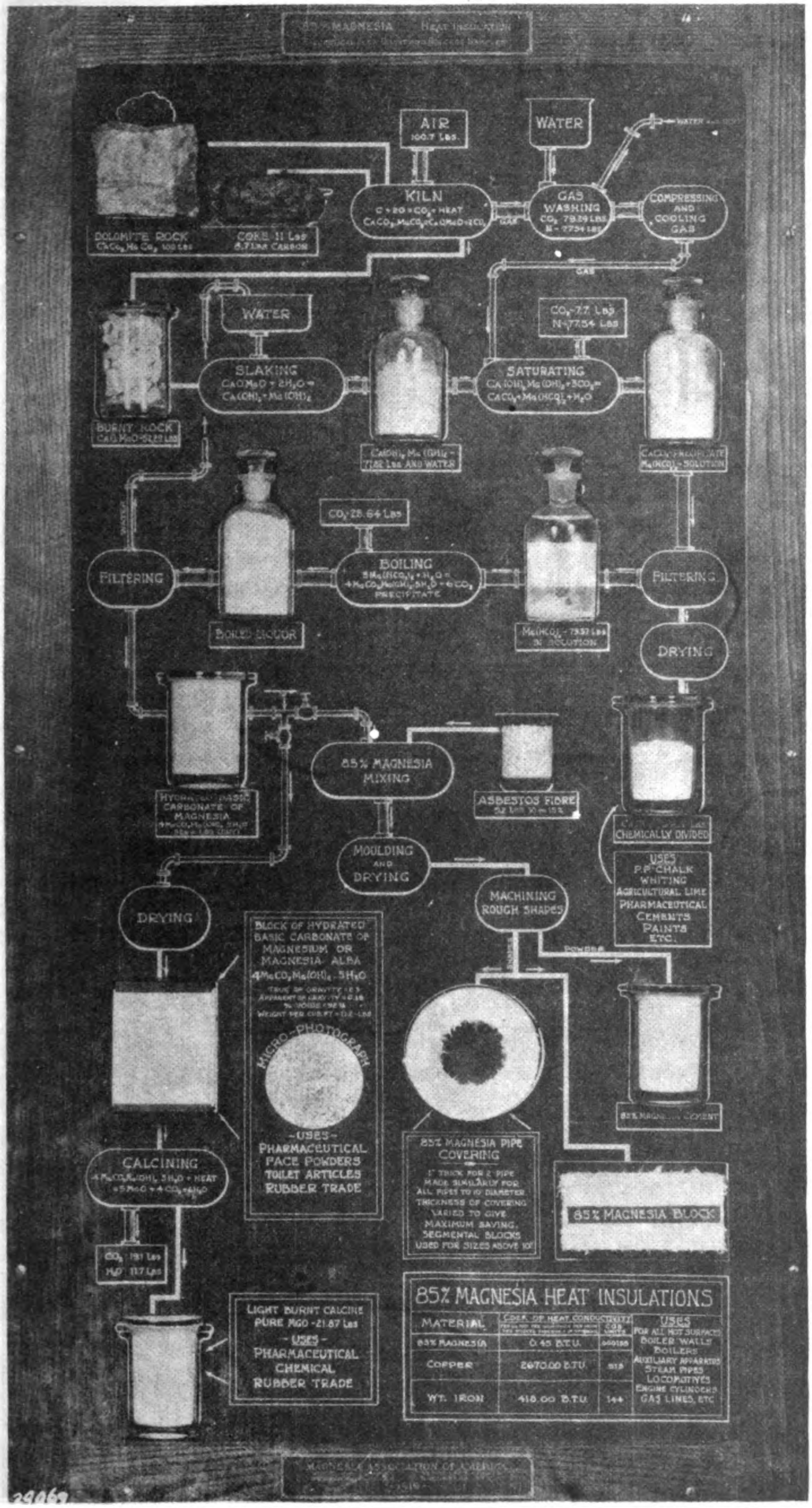

Figure 1.- Flow sheet showing processing of dolomite by the Pattinson method

Imports, 1919 to 1929

Calendar year	Quantity, pounds	Value	Value per pound
1919	5,094	$ 1,101	$ 0.216
1920	14,930	1,512	.101
1921	18,514	2,061	.111
1922	36,254	3,385	.093
1923	1,046,990	55,137	.053
1924	481,439	25,333	.053
1925	190,413	13,004	.068
1926	241,293	16,142	.067
1927	348,383	20,115	.058
1928	283,264	17,512	.062
1929			

The principal source of imports is England; smaller quantities are derived from Germany.

The duty since 1913 on carbonate of magnesia has remained at 1½ cents per pound. Under the Act of 1930 (par. 49) provision is made for manufactures of carbonate of magnesia, dutiable at 2 cents per pound.

Exports

Statistics of exports are not available.

Markets and Prices

Wholesale prices of domestic magnesium carbonate precipitated, technical grade, in the New York market have remained fairly steady at 6 cents per pound for several years. From January, 1923, to April, 1925, the price was 8 cents. During the World War a maximum of about 20 cents was reached. Previous to 1916 prices ordinarily ranged between 4 and 6 cents, delivered in New York.

Eighty-five per cent carbonate of magnesia pipe coverings and magnesia blocks are sold on the basis of standard price lists adopted August 1, 1907. Discounts recently averaged approximately 50 per cent off this list. For an ordinary 2-inch pipe the cost of a 1 1/32-inch covering, so-called "standard covering" with canvas jacket, is 36 cents as listed or approximately 18 cents after deducting the discount. For a 2-inch covering for the same size of pipe the price less discount is 50 cents per square foot. Carbonate of magnesia blocks for covering boilers and similar surfaces are furnished in standard sizes either 6 by 36 inches or 3 by 18 inches. The list price for such blocks 1 inch thick is 30 cents per square foot.

MAGNESIUM SULPHATE

Description and Uses

Magnesium sulphate or Epsom salts occurs in the mineral kieserite, $MgSO_4 \cdot H_2O$, in the Stassfurt salt beds and as epsomite, $MgSO_4 \cdot 7H_2O$, in the gypsum quarries of Montmartre, in Spain, in Chile, and in the Mammoth Cave, Ky.[8] Epsomite has also been found in the United States in California, Colorado, New Mexico, Tennessee, Utah, Washington, and Wyoming. Kieserite occasionally forms rhombic prisms but usually occurs in granular masses. Epsomite is found massive and also in silky or long, needle-shaped crystals. Magnesium sulphate forms the purgative principle of bitter spring waters such as those of Bath, England, and Seidleitz, Saidschuetz, and Puellna in Bohemia.

The salt with 7 molecules of water--variously described as Epsom salts, bitter salt, Lemery's salt, salts of England, etc.--forms small odorless, colorless prisms or needles; has a bitter, saline taste; and is soluble in water but insoluble in alcohol. The melting point is 70° C., and at 150 to 160° C. it loses 6 molecules of water and at about 280° C. it becomes anhydrous. The anhydrous salt is a heavy, white, amorphous powder which is insoluble in water and even in dilute acids; it melts at about 1,580° C. The specific gravity is 4.4 as compared with 1.7 for the normal hydrated salt.

Probably the largest use for the purified magnesium sulphate is in the drug trade and in the manufacture of laxative mineral waters. The commercial grade is used for sizing textiles, and for weighting silks, paper, and leather. Some of its minor uses are in connection with the manufacture of poultry feed, bath salts, dry colors, printing inks, and standardizing dyes. A solution of magnesium sulphate is used in the manufacture of artificial silks by the viscose process. According to a report from United States Consul Claiborne[9] in Germany, 4 to 4½ tons of the salt is consumed for every ton of finished rayon; hence a large factory may use 45 tons in one day.

Methods of Production

Magnesium sulphate is made by dissolving magnesite or dolomite in sulphuric acid, with subsequent crystallization. It is also made extensively in the United States from natural salt brines in Michigan. Deposits of natural epsomite have also been utilized, the salt being purified by recrystallization. In Germany it is manufactured on a large scale from kieserite.

At Stassfurt the crude kieserite is obtained chiefly from the upper beds (Abraumsalz). Since it is only sparingly soluble it is first washed with water to remove the chlorides of magnesium and sodium. The salts are suspended on large sieves standing in tanks of water and the kieserite powder falls through the meshes of the sieves. Gangue and other impurities, including anhydrite and large lumps of rock salt, remain behind on the sieves. The kieserite powder after being washed with water is packed in conical wooden molds, in which it sets to a compact mass containing 80 to 90 per cent of Epsom salts and only 1 or 2 per cent of sodium chloride. A large quantity of such material is marketed, but the remainder is purified by recrystallization and sold as Epsom salts. The process of producing magnesium sulphate from magnesium chloride bitterns or tachydrite, a mixture of calcium and magnesium chlorides, has been described by the late president of the Dow Chemical Co.[10]

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[8] Thorpe, Sir Edward, Dictionary of Applied Chemistry; Vol. 4, 1922, p. 193.

[9] Claiborne, Hamilton C., World Trade Notes on Chemicals and Allied Products: U. S. Department of Commerce, vol. 2, May 21, 1928, p. 2.

[10] Dow, Herbert H., Economic trend in the chemical industry: Ind. and Eng. Chem., Feb., 1930, pp. 115-116.

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Sulphur dioxide gas is absorbed in magnesium hydroxide to form magnesium sulphite or magnesium acid sulphite. This mixture is then oxidized to sulphate by blowing with air. We found that the acidity or alkalinity--or in other words, the hydrogen-ion concentration--of the magnesium sulphite solution was of utmost importance in carrying out the oxidation. It is well known that the oxidations of salts of lime, magnesium, iron, manganese, etc., are most easily attained in an alkaline medium, as in the re-oxidation of manganese salts in the Weldon process. In the present case, however, although an alkaline condition would be desirable for effecting the oxidation, the magnesium sulphite unfortunately is almost insoluble in an alkaline solution and consequently would escape oxidation at a satisfactory rate when the suspension was blown with air. On the other hand, magnesium acid sulphite is readily soluble, but the acidity of the solution retards and may even stop the oxidation completely. In this dilemma we were finally led to a solution of the problem by the discovery that a mixture of normal sulphite and acid sulphite within a narrow range of composition could be oxidized at a sufficiently rapid rate to make the process commercially feasible. It was important, however, to maintain the composition of mixture within the prescribed limits, if the oxidation were to be effected successfully.

At this point the question arose--how to maintain the correct ratio of normal sulphite to bisulphite, when the proportions were constantly changing as the oxidation proceeded. Chemical analysis and control were hopeless. In the first place the mixture was of a muddy consistency, hard to filter, and incapable of showing a good end point with any known indicator. Then again, if a suitable indicator could have been found which would have made possible a sufficiently accurate titration, the usual methods of chemical analysis would have been too slow. Before the results could have been obtained, the composition of the mixture would have changed materially. However, the optimum ratio of normal sulphite to acid sulphite corresponds to a certain definitely acidity of the solution--that is, to a definite hydrogen-ion concentration. By devising an instrument which would record almost instantaneously the hydrogen-ion concentration of the mixture in the oxidation tank, it became possible to follow the progress of the reaction closely and to maintain the correct hydrogen-ion concentration by suitable additions of magnesium hydroxide. Although the development of a satisfactory recorder required more time than was anticipated, the object was successfully accomplished. Now it has been so far improved that the recorder is caused to actuate a motor-operated valve which controls the feed of magnesium hydroxide added to the liquor. The whole operation of controlling the progress of the oxidation and the proper additions of hydroxide to maintain the correct acidity is carried out automatically. When the batch is finished, requiring about 8 hours, a workman opens a valve to empty the tank and then refills with fresh mixture to start the next batch. At other times no operating labor is required except for occasional inspection. The automatic recorder functions accurately and without sleeping. It is not going too far to say that this process would have been a failure but for the creation of automatic recording and control means, which have proved to be indispensable for maintaining the uniform conditions required for successful operation.

Each one of the four vital factors in labor-saving in a chemical plant is well exemplified in the Epsom salt process. We use equipment of such size that it can run for an 8-hour period before dumping the batch. The analysis of the batch is automatically recorded continuously, presenting on a chart clear history of the progress of the reaction. The automatic analyzer is employed to actuate valves to control the flow of materials added to the batch. Finally the complete cycle of the process is carried out continuously and automatically without manual operation of any kind except to open a valve to dump the finished batch. In fact, it would no doubt require the exercise of but a little more ingenuity to contrive means to control the valves for emptying and refilling the tank, thus dispensing entirely with manual labor or operation. Perhaps we will come to that, but we are still old-fashioned enough to believe that a process should have some one to look after it, at least once in every 8 hours.

Domestic Production

In the United States magnesium sulphate is produced principally by five companies, one each in Michigan, Illinois, Ohio, Pennsylvania, and Georgia. From time to time the magnesium salt deposits near Oroville, Okanogan County, Wash., owned by the Magnesium Products Co. of Portland, Oreg., have been operated, but in the last few years these deposits have not been productive, although sales of refined Epsom salts have been made by the company locally and in western Washington. A deposit, said to contain at least 1,000 000 tons of epsomite, is reported to be in San Bernardino County, Calif., about 28 miles from Searles Lake, and it has been proposed to treat this material with trona to produce magnesium carbonate and Glauber's salts. At present, however, it appears that the only magnesium sulphate produced from natural salts and bittern waters in the United States is the product of the Dow Chemical Co. at Midland, Mich.

The total domestic output from all sources is reported by the Bureau of the Census as follows:

Total domestic output of magnesium sulphate from all sources[1]

Year	Short tons	Value	Year	Short tons	Value
1914	14,633	$297,000	1923	20,676	$851,103
1919	29,348	1,497,000	1925	23,428	1,219,177
1921	14,923	753,822	1927	27,665	1,141,633

[1] Reported by Bureau of the Census.

Imports

Prior to the war the imports of magnesium sulphate ranged from 3,631,2 pounds in 1908 to 13,549,599 pounds in 1914. As imports were cut off by the World War, the quantity dropped to only 2,045 pounds in 1918. Imports since 1919 have come chiefly from Germany and are shown below. According to the

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United States Tariff Commission[11] a comparison of the unit values of domestic production and imports indicates that the domestic production is mainly of the U. S. P. grade, whereas imports consist mainly of the commercial or technical grade.

The Tariff Act of 1922 increased the duty on magnesium sulphate from 1/10 cent per pound to ½ cent per pound. Under the Act of 1930 (par. 49) the rate is 3/4 cent per pound.

Imports of magnesium sulphate, 1919-1929

Calendar Year	Pounds	Value	Value por pound
1919	17,647	$1,473	$0.083
1920	1,803,769	66,944	0.037
1921	12,519,778	88,153	0.007
1922	25,390,734	200,203	0.008
1923	14,455,920	71,566	0.005
1924	8,881,181	57,579	0.006
1925	8,211,228	50,466	0.006
1926	10,600,582	61,018	0.006
1927	11,620,675	60,527	0.005
1928	10,459,596	61,600	0.006
1929	13,541,189	82,416	0.006

Exports

Statistics of exports are not available.

Prices

Epsom salts of technical grade were quoted in New York at $1.70 per 100 pounds throughout the greater part of 1928. This price was continued through 1929 and into 1930. In August, 1930, domestic technical grade in bags or barrels was quoted at $1.70 to $1.90, and the U.S.P. grade at $2.15 per 100 pounds in bags and $2.25 in barrels (car lots). Imported material of U.S.P. quality was quoted at $1.90 and $2.

CALCINED MAGNESIA OR MAGNESIA OXIDE

Description and Uses

Calcined magnesia is a variety of magnesium oxide formed by heating the precipitated carbonate at a moderately high temperature. It is a white, fluffy powder, insoluble in water but soluble in acids. The medicinal grade must conform to specifications of the United States Pharmacopoeia and is used chiefly as an antacid in pharmaceuticals (milk of magnesia). It is also used in toilet preparations. The technical grade is used as an insulating material and in compounding rubber. For certain purposes specially selected magnesite may be used, and such material may be described as "calcined magnesia, heavy."

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[11] U. S. Tariff Commission, Summary of Tariff Information, 1929, Schedule 1, p. 245.

For other grades the raw material is virtually the same as the basic carbonate used by the 85 per cent magnesia insulation manufacturers. The use of calcined magnesia as an accelerator in rubber is said to be decreasing.

Magnesia is generally obtained by gentle but prolonged heating of the carbonate. About 2½ pounds of technical precipitated carbonate is required to produce 1 pound of calcined magnesia. The carbonate begins to decompose at about 300° C., but the calcining temperature must be considerably higher. The specific gravity is normally 3.07 to 3.2 but may be increased to 3.61 by continued heating.

Domestic Production

Available statistics of production in the United States are as follows:

Domestic production of calcined magnesia, 1919-1925

Year	Pounds	Value
1919	9,031,650	$1,176,858
1921	2,648,678	141,340
1923	13,193,112	707,975
1925	11,086,480	640,836

Imports

Before the war imports of calcined magnesium fluctuated from less than 50,000 to more than 110,000 pounds annually. Since 1922 imports have generally increases. A maximum of 520,394 pounds was reached in 1926 but the value per pound in that year being substantially below normal, the maximum value was reached in 1929 when 471,545 pounds valued at $83,866 were imported. The imports are derived mainly from England and to a less extent from Germany.

Imports of calcined magnesia, 1919-1929

Calendar Year	Pounds	Value	Value per pound
1919	22,637	$11,358	$ 0.502
1920	26,859	9,093	.339
1921	35,182	7,593	.216
1922	96,792	15,969	.165
1923	141,375	30,802	.218
1924	101,998	29,252	.287
1925	162,790	43,356	.266
1926	520,394	51,454	.099
1927	259,357	48,093	.185
1928	300,897	60,325	.200
1929	471,545	83,866	.178

The duty on magnesium oxide or calcined magnesia was 3½ cents per pound under the Tariff Acts of 1913 and 1922 but was increased to 7 cents per pound under the Act of 1930 (par. 49).

Exports

No data are available on exports.

Prices

The selected magnesite, sold as calcined magnesia, heavy, is generally worth 4 cents or more per pound. The U.S.P. grade, heavy, generally sells for about 50 cents. The standard light calcined magnesia (U.S.P.) which sold in 1929 at 45 to 60 cents a pound broke early in April to 25 to 30 cents a pound.

MAGNESIUM CHLORIDE

Description

Magnesium chloride is highly soluble in water and has a sharp, bitter taste. It crystallizes usually with 6 molecules of water ($MgCl_2 \cdot 6H_2O$) in prismatic or "chunky" forms (monoclinic system). This salt becomes entirely fluid when heated to 118° C., but even at 105° it loses some hydrochloric acid. It is impossible to prepare the anhydrous salt by simple heating. About one-third of the water may be expelled without carrying off chlorine, but the tendency to form basic salts can be prevented only by carrying on the dehydration in an atmosphere containing ammonium chloride, hydrochloric acid, or other substance that inhibits the loss of chlorine. E. Solvay, however, patented a process for heating the hexahydrated salt at 120° C. until 80 per cent of water was expelled, leaving a residue which could be further heated without much loss of hydrochloric acid.

Anhydrous magnesium chloride forms white transparent masses of large lustrous crystals of 2.177 specific gravity. The melting point is about 708° C. and the salt may be distilled in a current of hydrogen forming a distillate which at first resembles butter but which on cooling forms a mass of crystalline plates.[12]

There are at least six different hydrates of magnesium chloride ranging from a 12-molecule salt to one containing only 1 molecule of water of crystallization (obtained only by passing dry hydrogen chloride over the tetrahydrated salt). The 6-molecule salt, however, is the one that crystallizes from aqueous solution between -3.4 and 116.67°; it occurs in the Stassfurt (Germany) deposits as the mineral bischofite. The salt is available in C.P. and N.F. grades, but the bulk of the consumption is in the technical grades, wherein it is furnished in the crystal, fused, flake, and powder forms. It has also been marketed extensively in the form of a concentrated solution or "liquid," but at present practically all the domestic product is sold in flake or powder form. In the flaking process some of the water of crystallization is removed. The following analysis is characteristic of the product of the leading American manufacturer:

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[12] Data mainly from Mellor, J. W., Treatise on Inorganic and Theoretical Chemistry; Vol. 4, London, 1923, pp. 300-305.

Original from THE OHIO STATE UNIVERSITY

	Per cent
$MgCl_2 \cdot 6H_2O$	103.5
$MgSO_4$	0.04
$CaCl_2$	0.24
NaCl	0.63
KCl	None

The imported product is likely to contain potassium chloride as an impurity.

All the solid salts of magnesium chloride are deliquescent, and they are also readily soluble in alcohol, combining directly with evolution of heat with methyl or ethyl alcohol to form alcoholates of magnesium chloride.

Numerous double salts of magnesium and other chlorides have been described. Of these probably the most important is carnallite, $KMgCl_3 \cdot 6H_2O$, which occurs in the Stassfurt and other salt deposits. Tachydrite, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$, a highly hygroscopic salt, likewise occurs naturally in the Stassfurt deposits and is also produced as an intermediate product in the evaporation of bitterns.

Uses

Anhydrous magnesium chloride is the raw material for the manufacture of metallic magnesium. The 6-molecule salt is used chiefly with calcined magnesite in the preparation of oxychloride (Sorel) cement, employed for floors, stucco, and to a more limited extent in other products, notably "magnesite lumber." Some of the minor uses[13] are in connection with the treatment of textiles (sizing, dressing, and filling of cotton and woolen fabrics, thread lubricant, wool carbonization), disinfectants, fire extinguishers, fire-proofing wood, refrigerating brines (due to non-splashing properties), ceramics, chilling drilling tools, paper manufacture, road dust-laying preparations, and floor-sweeping compounds. The magnesium chloride liquors remaining after the extraction of common salt are also used as sources of magnesium sulphate and other compounds, including the technical carbonate and magnesia.

Methods of Production

Magnesium chloride may be made by treating magnesite (either crude or caustic calcined) with hydrochloric acid, and it can also be prepared by cooling a concentrated solution of magnesium sulphate and sodium chloride in a manner such that sodium sulphate crystallizes out, leaving magnesium chloride in solution.

The bulk of the world supply, however, is derived from residual liquors from the extraction of potash (in Germany) or common salt. At Stassfurt the hydrated salt is recovered after extracting potassium chloride by evaporating the mother liquor until its specific gravity is about 1.375 and then cooling and crystallizing. The crystals may be melted at about 400° C. forming a partly dehydrated mixture containing some oxychloride. In Michigan the magnesium chloride is present in the waters from salt wells. The brine (which contains approximately 14 per cent NaCl, 9 per cent $CaCl_2$, 3 per cent $MgCl_2$, and 0.15 per cent bromine)

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13 - The Condensed Chemical Dictionary, Chemical Catalog Co., New York, 1930, p. 293.

is first treated for bromine and then treated with a magnesium hydrate slurry to precipitate the iron and other impurities which are separated in continuous thickeners and sedimentation tanks. The decanted liquor is then evaporated (using exhaust steam) until the NaCl has crystallized and the salt is removed on rotary filters. The $MgCl_2$ and $CaCl_2$ in the mother liquor are next separated from each other by fractional crystallization. According to Gann:[14]

> In practice this is accomplished by concentrating a solution with a 1 : 3 weight ratio of $MgCl_2$ to $CaCl_2$ whereupon crystals of the double salt "Tachydrite" are formed. The composition of this salt is represented by the formula--$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$. It has a 2 : 1 ratio of $MgCl_2$ to $CaCl_2$, but its crystals are in equilibrium with a mother liquor having a $MgCl_2$ to $CaCl_2$ ratio of 1 : 10. The crystals and liquor are separated in false bottom tanks. This $CaCl_2$ rich solution and wash water from the Tachydrite are reworked elsewhere to give $CaCl_2$ and Epsom salts. The Tachydrite crystals are then dissolved in hot water and the solution transferred to a series of crystallizers where substantially pure $MgCl_2 \cdot 6H_2O$ separates, leaving a mother liquor containing $MgCl_2$ and $CaCl_2$ in a ratio of approximately 1 : 1. This solution, together with the $MgCl_2 \cdot 6H_2O$ wash water, contains approximately half of the $MgCl_2$ originally present in the brine and is returned to the process for reworking***. In order to facilitate further treatment, the $MgCl_2 \cdot 6H_2O$ crystals are melted in their water of crystallization and the fused mass is flaked on rotating steel drums.

In order to use this material in the electrolytic cells for the manufacture of magnesium metal, it must be dehydrated. Carefully controlled air-drying on the countercurrent principle produces a composition corresponding approximately to $MgCl_2 \cdot 2H_2O$, and the last 2 molecules of water are removed by heating to still higher temperature in an atmosphere of HCl, which prevents hydrolysis and the formation of MgO.

The mixture of calcium and magnesium chlorides may also be treated with calcined dolomite or magnesite, precipitating a hydrate of magnesia and a solution of calcium chloride. It has also been proposed to remove the calcium from the solution as a sulphate.

In Germany anhydrous chloride for the manufacture of magnesium metal is made by the interaction between magnesium oxide and chlorine gas in the presence of carbonaceous matter.

Domestic Production

Magnesium chloride was not produced in the United States until after the outbreak of the World War, but when imports from Germany were cut off, a large domestic industry was developed, chiefly as an offshoot of the salt industry in Michigan and California. As there are generally less than three producers, the Bureau of Mines has not been at liberty (in most years) to publish production figures separately. The latest figures that can be published relate to 1926, when the total sales of flake chloride amounted to 45,630,000 pounds valued at $674,680 (1.48 cents a pound); in addition 6,939,000 pounds of chloride were produced in liquid form, ranging from 23 to 36° B., that was sold as road liquor at an average price of 0.39 cents a pound. In that year the output came from four companies--Arden Salt Works, Arden, Calif.; California Chemical Co., Chula Vista, Calif.; Dow Chemical Co., Midland, Mich.; and the Oliver Salt Co., Mount Eden, Calif.

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[14] Gann, John A., The Magnesium Industry: Am. Inst. Chem. Eng., Detroit Meeting, June 4-6, 1930, p. 7.

Imports

Germany is the chief source of imports. Statistics are given in the following table:-

Imports of magnesium chloride

Year	Quantity, pounds	Value
	Magnesium Chloride	
1919	11,200	$ 537
1920	454,334	7,098
1921	7,365,812	85,727
1922 (Jan. 1 - Sept. 21)	7,021,954	71,846
	Magnesium Chloride, n.s.p.f.	
1922 (Sept.22 - Dec. 31)	4,381,344	41,745
1923	22,996,275	188,045
1924	15,064,351	83,386
1925	15,922,254	105,462
1926	16,093,867	110,477
1927	8,140,989	59,635
1928	5,799,750	41,712
1929	3,291,856	23,120
	Magnesium Chloride, Anhydrous	
1922 (Sept.22 - Dec. 31)	539	27
1923	56,110	2,703
1924	136,082	1,820
1925	- - -	- - -
1926	- - -	- - -
1927	44,374	315
1928	- - -	- - -
1929	- - -	- - -

Exports

Statistics of exports are not available.

Foreign Production

Production in Germany increased from 88,184,000 pounds of the solid and liquid forms in 1913 to 176,368,000 pounds in 1926, equal to three times the production in the United States.[15] In 1929 the German output was about 35,000 tons of solid salt and about 60,000 tons of liquor having an aggregate value of 3,700,000 marks. British India is another large producer. In 1909 Italy produced 3,252,480 pounds [16] of magnesium chloride.

Markets and Prices

As a result of the declining use of magnesite cements in recent years, the demand for chloride for flooring and stucco has undoubtedly fallen off substantially from the high figures registered between 1923 and 1926. The domestic market formerly supplied principally by imports has recently been supplied mainly by domestic production.

The price of flake chloride in barrels f.o.b. domestic works has been $36 to $37 per short ton for five years or more. Imported chloride, fused, in barrels, was quoted around $26 a ton in 1924-25 but since May 1926 has been selling generally for about $31.75 to $33.50 in New York. Domestic fused chloride usually sells for about $2 a ton less than flake but higher than the imported material. As previously noted domestic chloride is purer and contains substantially more $MgCl_2$ than the German product.

MINOR COMPOUNDS[17]

A great variety of magnesium salts are of more or less commercial importance. Most of these minor compounds are used exclusively in medicine but a number of them have other uses. The borate, $3MgO.B_2O_3$, is used as a preservative. The nitrate, $Mg(NO_3)_2.6H_2O$, is used in pyrotechnics. The oleate, perborate and stearate are used in varnish driers; the stearate is quoted regularly in trade journals, the price in August, 1930, being 24½ to 26 cents a pound in barrels. The bromate, $Mg(BrO_3)_2.6H_2O$, and the formate, $Mg(CHO_2)_2.2H_2O$, are listed as laboratory reagents (the latter is also used in medicine).

Magnesium fluoride, MgF_2, is employed in ceramics and the silico fluoride (fluosilicate), $MgSiF_6$ (crystals or solution), is employed as a concrete hardener. In August, 1929, magnesium silicofluoride was quoted at 9 3/4 to 10 1/4 cents a pound (in barrels). Magnesium silicate, $3MgSiO_3.5H_2O$, is used extensively in the rubber industry, in paints and varnishes (as a pigment and filler), in glass and clay wares, in refractories, in the manufacture of permanently dry resins and resinous compositions, and as a bleaching agent for animal and vegetable oils; it may be made by the interaction of a magnesium salt and sodium silicate but much of the product sold as magnesium silicate is natural talc pulverized.

Magnesium hydroxide, made by precipitating a solution of any of the salts by means of sodium hydroxide, is used in sugar refining as well as in

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15 - U. S. Tariff Commission, Summary of Tariff Information, Schedule 1, Chemicals, Oils, and Paints, 1929, p. 244.
16 - U. S. Tariff Commission, Tariff Information Survey, A-10, 1921, p. 47.
17 - Data on uses taken mainly from the Condensed Chemical Dictionary, 2nd edition, 1930.

medicine. It may also be used as a source of magnesium oxide. In nature, the hydrate occurs as the mineral, brucite, a large deposit of which has been developed in Nevada.

The peroxide (magnesium perhydrol), MgO_2, is a general bleaching and oxidizing agent and is used especially in bleaching woolen and silk fabrics and as an antiseptic. It is made from sodium or barium peroxide and magnesium sulphate (in concentrated solution) and is sold in drums at about $1.15 a pound (August, 1930) f.o.b. works.

Magnesium tungstate, produced from magnesium sulphate and ammonium tungstate, is used in luminescent paints and in fluorescent screens for X-ray work.

Calcium-magnesium chloride is used instead of calcium chloride for dust-laying on roads, in freezing mixtures, etc.

Among the numerous minor medicinal compounds of magnesium regular quotations are available for hypophosphite $Mg(H_2PO_2)_2.6H_2O$ ($1.15 to $1.20 in cans, August, 1930). The following may also be listed as being used more or less commonly in medicine: Magnesium-ammonium phosphate, $MgNH_4PO_4.6H_2O$; acid magnesium phosphate, $MgH_4(PO_4)_2$; phosphate, $MgHPO_4.3H_2O$; glycerophosphate, $MgPO_4.C_3H_5(OH)_2$; lactophosphate (45 per cent magnesium lactate); lactate, $Mg(C_3H_5O_3)_2.3H_2O$; benzoate, $Mg(C_7H_5O_2)_2$; borocitrate; citrate, $Mg_3(C_6H_5O_7)_2.14H_2O$; iodide, $MgI_2.8H_2O$; salicylate, $Mg(C_7H_5O_3)_2.4H_2O$; and sulphite, $MgSO_3.6H_2O$.

LIST OF MANUFACTURERS

Magnesium Carbonate, Technical

Keasbey & Mattison Co., Ambler, Pa.
Ehret Magnesia Mfg. Co., Valley Forge, Pa.
Norristown Magnesia & Asbestos Co., Norristown, Pa.
Philip Carey Mfg. Co., Lockland, Ohio.
Los Angeles Chemical Co., 2200 Santa Fe Ave., Los Angeles, Calif.
Celite Products Co., 840 Monodnock Bldg., Chicago, Ill.
Johns-Manville, Inc., Madison Ave. and 41st St., New York, N. Y.

Epsom Salts

Victor Chemical Co., Chicago Heights, Ill.
Dow Chemical Co., Midland, Mich.
Coca-Cola Co., Atlanta, Ga.
Drackett Chemical Co., 5020 Spring Grove Ave., Cincinnati, Ohio.
General Chemical Co., 40 Rector St., New York, N. Y.
Pacific Silicate Co., Matson Bldg., San Francisco, Calif.
Magnesium Products Co., Portland, Oreg. (Natural magnesium sulphate deposits at Oroville, Wash.)

Calcined Magnesia

Keasbey & Mattison Co., Ambler, Pa.
Philip Carey Mfg. Co., Lockland (Cincinnati), Ohio.
General Magnesite & Magnesia Co., Venango and Balfour Sts., Philadelphia, Pa.

Magnesium Chloride

Dow Chemical Co., Midland, Mich.
California Chemical Corp., San Francisco, Calif.

General[18]

J. T. Baker Chemical Co., Philipsburg, N. J.
A. Daigger & Co., 159 W. Kinzie St., Chicago, Ill.
Henry A. Golwynne, 26 Cortlandt St., New York, N. Y.
Innis, Speiden & Co., Ind., 117 Liberty St., New York, N. Y.
Merck & Co., Inc., Rahway, N. J.
Schofield-Donald Co., Inc., 154 Nassau St., New York, N. Y.
McKesson & Robbins, Inc., 79 Cliff St., New York, N. Y.
Wishnick-Tumpeer, Inc., 251 Front St., New York, N. Y.
Harshaw Chemical Co., Cleveland, Ohio.
Speiden-Whitfield Co., Inc., 150 Nassau St., New York, N. Y.
Jungmann & Co., Inc., 155 Sixth Ave., New York, N. Y.
Roessler & Hasslacher Chemical Co., 10 E. 40 St., New York, N. Y.
Whittaker, Clark & Daniels, Inc., 245 Front St., New York, N. Y.

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[18] - Includes importers and dealers.